Première loi de la thermodynamique: détermination du coefficient Joule-Thomson pour différents gaz

Rédigé par Pierre-Alexandre Turgeon

Introduction

L'énergie d'un gaz parfait est indépendante du volume et de la pression, elle ne dépend que de la température. En conséquence, la température d'un gaz idéal soumis à une expansion adiabatique demeure inchangée dans le processus. En revanche, en 1854 James Prescott Joule et William Thomson (aussi connu sous le nom de Lord Kelvin) ont démontré que la température d'un gaz réel changeait dans une expansion adiabatique. Ce phénomène connu sous le nom d'effet Joule-Thomson est aujourd'hui largement utilisé dans la liquéfaction des gaz. Pour comprendre cet effet, il faut tenir compte du comportement non-idéal des gaz en introduisant des paramètres comme les interactions intermoléculaires et le volume des particules. Cette non-idéalité se traduit par un coefficient Joule-Thomson propre à chaque gaz.

Vous aurez à mesurer le coefficient Joule-Thomson de 3 gaz différents, soit l'hélium, le dioxyde de carbone et l'azote. Cette expérience vise à vous familiariser avec différentes techniques expérimentales telles que la manipulation de gaz comprimés, l'acquisition de données par ordinateur ainsi que l'utilisation de thermocouples et de capteurs de pression. Le montage expérimental que vous utiliserez devra être assemblé par votre équipe avant de pouvoir effectuer les mesures. L'ensemble de la théorie reliée à l'expérience de détermination du coefficient Joule-Thomson se trouve dans les documents complémentaires cités à la fin de ce protocole, principalement dans l'ouvrage de Garland, Nibler et Shoemaker. Pour cette raison, elle ne sera pas exposée plus en détail dans le présent document.

Appareillage

Pour réaliser vos mesures, vous aurez à votre disposition un capteur de pression électronique, des thermocouples, une carte d'acquisition ainsi qu'un amplificateur de voltage. Ces appareils sont peut-être nouveaux pour vous, c'est pourquoi ils seront brièvement décrits dans le protocole.

Capteurs de pression WIKA A-10

Les capteurs de pression WIKA fonctionnent grâce à l'effet piézorésistif. Vous êtes peut-être familiers avec l'effet piezoélectrique grâce auquel une pression appliquée sur un cristal génère une différence de potentiel. Dans le cas de l'effet piézorésistif, la pression appliquée sur un semi-conducteur mène plutôt à un changement dans la résistance. Les capteurs sont

conçus pour donner un signal de sortie allant de 0 à 10V en fonction de la pression appliquée. Ceux qui seront mis à votre disposition auront une plage de réponse linéaire allant de 0 à 160 PSIG (PSIG: PSI par rapport à la pression atmosphérique). Par exemple, un signal lu de 0 V correspondra à la pression atmosphérique alors qu'un signal lu de 3.48 V correspondra à 58.5 PSIG. Pour vos analyses, vous devrez convertir le voltage en pression à l'aide des informations précédentes. L'unité SI de pression est le bar, alors vous aurez à effectuer une conversion. Veuillez prendre note que le capteur de pression peut avoir un décalage (*offset*), ce qui aura pour conséquence que le voltage ne sera pas exactement de 0V à pression ambiante. Vous devrez en tenir compte dans le traitement de vos données.

Pour fonctionner, les capteurs de pression ont besoin d'une source d'alimentation 24VDC. Vous devrez donc connecter le petit transformateur dans une des fiches d'alimentation située sur votre espace de travail.

Thermocouple type T (Cuivre/Constantan)

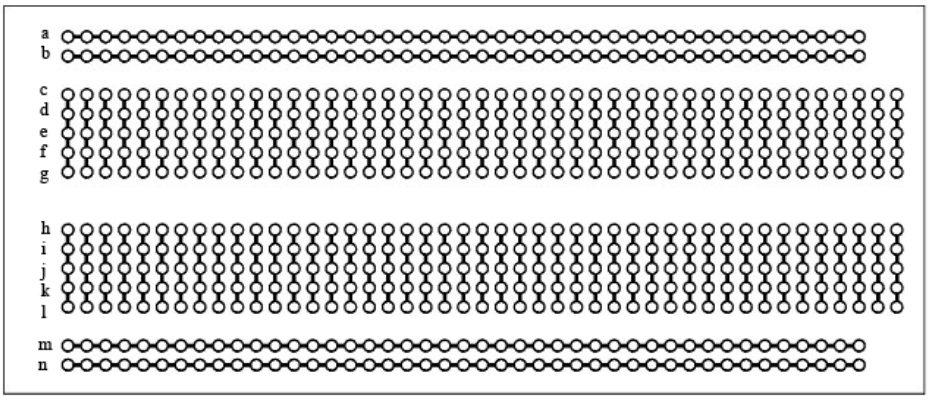
Résumé de façon simple, un thermocouple est la jonction physique entre deux métaux ou deux alliages différents. Cette jonction génère un potentiel (appelé potentiel de jonction) dont la valeur dépend de la température. En mesurant ce potentiel par rapport à une référence, la température de la jonction peut être déterminée avec une assez bonne précision. Le thermocouple est l'un des outils de mesure de température le plus utilisé puisqu'il est peu coûteux, durable et qu'il est généralement assez sensible. Dans l'expérience de détermination du coefficient Joule-Thomson, deux thermocouples seront mis en série, de sorte que la différence de potentiel mesurée entre les deux jonctions sera directement proportionnelle à la différence de température des deux jonctions. Le fait de faire une mesure "différentielle" à deux thermocouples nous permet d'éviter l'utilisation d'une référence externe. Les thermocouples de type T (cuivre/constantan) ont une réponse d'environ 39 µV/K. Une charte détaillée du voltage en fonction de la température est incluse à la fin de ce document. Comme le signal est relativement faible, il faudra l'amplifier à l'aide d'un circuit électrique qui est détaillé ci-dessous

Circuit d'amplification thermocouple

Comme mentionné précédemment, le signal généré par le thermocouple est très faible : 39 µV/K, soit $4x10^{-5}$ V/K. Pour amener ce signal à un niveau acceptable, il vous faudra construire un circuit d'amplification. Le circuit sera construit sur un *breadboard*, une petite plaque qui permet de connecter les composantes sans les souder. La figure à la page suivante représente les connections à l'intérieur du *breadboard*. Le rail a servira à l'alimentation positive alors que le rail n servira à l'alimenation négative. Les rails b et m seront reliés à la terre (ground) et vous devrez vous-même les relier ensembles. Les composantes seront disposées sur les rails intermédiaires de c à l.

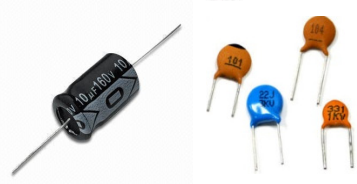
L'alimentation du circuit sera fournie à l'aide de deux batteries de 9V que vous devrez connecter en série. Une fois votre circuit complété, vous devrez connecter la borne

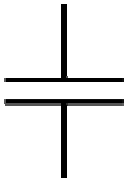
positive de la batterie 1 sur le rail a du *breadboard*, la borne négative de la batterie 1 sur le rail b, la borne positive de la batterie 2 sur le rail m et la borne négative de la batterie 2 sur le rail n. Comme mentionné plus haut, les rails b et m devront être reliés ensembles.



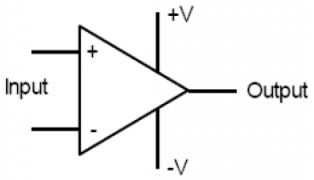
Votre circuit comprendra plusieurs types de composantes électroniques dont certaines que vous connaissez déjà. Tout d'abord, la résistance, avec un code de couleur qui permet de déterminer sa valeur. Pour connaître la valeur de la résistance plus rapidement, vous pourrez utiliser votre multimètre Keithley qui comprend une option pour la mesurer. L'image ci-contre vous donne un exemple de ce à quoi ressemble une resistance et vous montre le symbole utilisé afin de noter une résistance sur un schéma électrique.

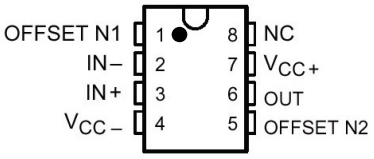
Il y a aussi des condensateurs de deux différents types : céramique et électrolytique. Les condensateurs céramiques (à droite dans la figure) peuvent être reliés dans n'importe quelle direction alors que les condenateurs électrolytiques (à gauche) sont polarisés et doivent être reliés dans la bonne direction. Les condensateurs électrolytiques ont deux extrémités différentes. L'extrémité de couleur noir doit être placée vers le côté le plus négatif du circuit alors que l'extrémité de couleur métallique doit être reliée au côté le plus positif. L'extrémité noire est aussi identifiée par un anneau noir sur l'enveloppe externe du condensateur. Le symbole d'un condensateur dans un circuit électrique est représentée ci-contre.





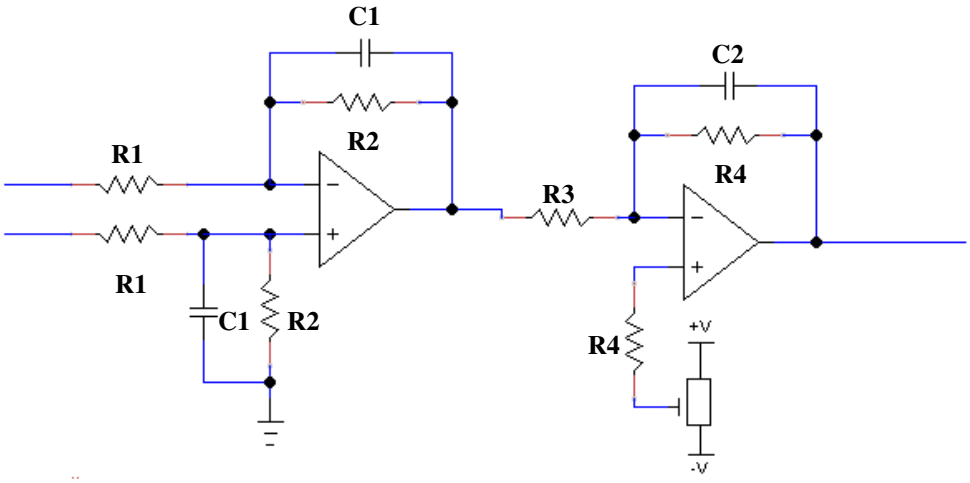
Finalement, il y aura des amplificateurs opérationnels qui permettront d'effectuer l'amplification de votre signal. L'amplificateur que vous utiliserez sera le TL071. Il sera représenté par le symbole triangulaire suivant dans le circuit électrique et ressemblera à la petite puce ci-contre. La connectivité de





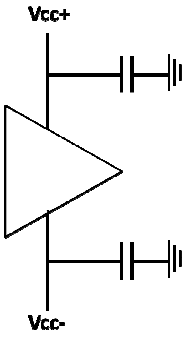
l'amplificateur opérationnel est représentée pour les connecteurs de 1 à 8, dans la réalité, vous n'aurez besoin que des connecteurs 2,3,4,6 et 7. Les amplificateurs opérationnels ont besoin d'être alimentés (Vcc-et Vcc+) pour fonctionner. Remarquez la présence du point noir ou du demi-cercle en haut de la puce. Ce symbole se retrouvera sur l'amplificateur et vous permettra de l'orienter correctement.

Voici donc le circuit que vous aurez à reproduire pour l'amplification de votre signal (le circuit détaillé est disponible en annexe):



Vous remarquerez la présence d'un potentiomètre en bas à droite du circuit. Celui-ci vous permettra de compenser le décalage (*offset*) du signal en ramenant près de 0 le voltage de base du système.

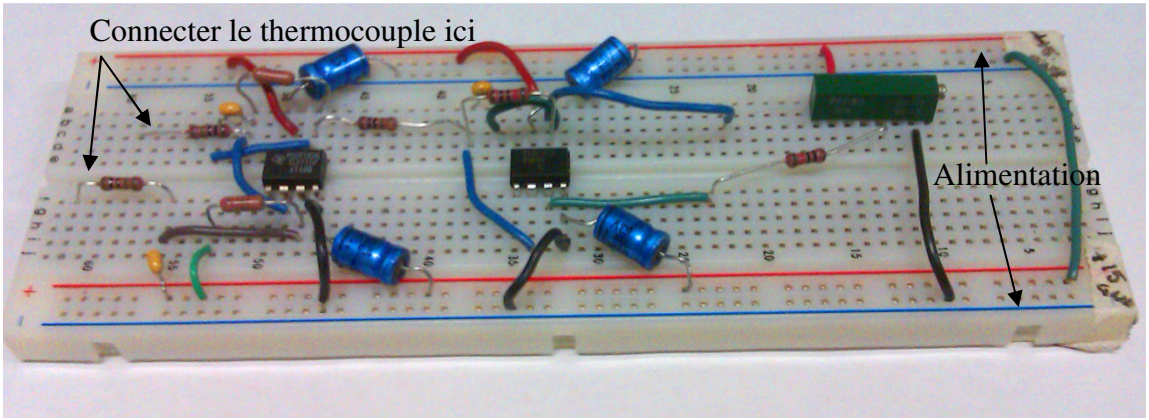
Le circuit peut être divisé en deux sections. La section de gauche amplifie d'abord le signal par un facteur de R2/R1. Dans votre cas, R2 a une valeur de 100 kΩ et R1 de 1 kΩ. Les condensateurs C1 servent à filtrer une partie du bruit électrique qui pourrait affecter votre circuit. Ils ont une capacité de 0.01µF. L'amplification de la première partie est donc d'un facteur 100. Pour la deuxième partie, l'amplification est déterminée par le facteur R4/R3. Dans ce cas, R4 est de 10 kΩ, R3 de 1 kΩ et C2 a une valeur de 0.001 µF. L'amplification de cette partie est de 10, et l'amplification totale de ce circuit est donc d'un facteur 1000.



L'alimentation des amplificateurs opérationnels doit être accompagnée de condensateurs de découplage. Ceux-ci permettent, encore une fois, de filtrer une partie du bruit qui pourrait affecter votre circuit. Vous devrez connecter des condensateurs électrolytiques pour relier chacune des bornes d'alimentation à la terre. Veillez à bien connecter les condensateurs dans la bonne direction (la direction ne sera pas la même pour les deux polarités de l'alimentation!). N'hésitez pas à demander de

l'aide à votre démonstrateur au besoin.

La photo ci-dessous est un exemple de circuit qui pourra vous aider à vous orienter dans le montage de votre circuit.



Veuillez prendre note que les amplificateurs opérationnels sont des pièces très fragiles et sensibles à l'électricité statique. Il est toujours conseillé de toucher une pièce de métal relié à la terre (par exemple, un boîtier d'ordinateur) avant de toucher aux composantes du circuit. Ceci permet d'évacuer l'électricité statique qui pourrait rester dans votre corps. Aussi, veuillez vous assurer d'avoir connecté les composantes correctement avant d'ajouter l'alimentation du circuit.

Carte d'acquisition Futek DAQ-0311A

La petite carte d'acquisition Futek permet de mesurer et d'enregistrer un signal électrique sur l'ordinateur en fonction du temps. Vous pourrez enregistrer la pression et la température de votre système pour ensuite effectuer l'analyse de vos données. Le modèle que vous utiliserez comporte trois entrées différentes, soit une entrée pour mesure différentielle et deux entrées pour des mesures par rapport à la terre (ground) qui agit comme référence. Vous utiliserez seulement les entrées référencées par rapport au ground. Cette carte permet l'acquisition entre -10V et 10 V avec une résolution de 16 bits. Elle a donc une gamme dynamique (dynamic range) de 20 V réparti en 16 bits (2^{16} possibilités). Sa plus petite mesure possible peut être calculée en divisant la gamme dynamique par le nombre de possibilités, on obtient donc 0.3 mV. La gamme dynamique de cette carte peut cependant être réduite, ce qui permet d'augmenter la résolution.

Montage expérimental

Le montage expérimental que vous allez utiliser est détaillé dans l'article qui se trouve en annexe à ce document (Halpern et Gozashti). Lorsque vous arriverez au laboratoire, le montage se trouvera en pièce détachées que vous devrez assembler par vous-même. Les différentes parties pourront s'assembler grâce à des connecteurs *Swagelok* que vous devrez serrer à l'aide du jeu de clés (wrench) qui vous sera fourni. Il est inutile de serrer trop fort les connecteurs.

Pour mettre le fritté d'acier inoxydable en place, il est suggéré de le placer entre deux joints toriques (o-rings). Ceci évitera des fuites de gaz sur les côtés du frité. Veuillez prendre des précautions avec les thermocouples puisque leur extrémité est fragile.

Déroulement de l'expérience

Vous devrez déterminer le coefficient Joule-Thomson de 3 différents gaz: hélium, dioxyde de carbone et azote. Pour y arriver, vous devrez vous-même trouver une façon de procéder (inspirez-vous des articles en annexe).

L'acquisition des données se fera entièrement avec la carte d'acquisition Futek ainsi que le logiciel d'accompagnement (FTezDAQ). Le logiciel est relativement simple d'utilisation et vous trouverez plus de détails dans le manuel d'utilisation (disponible sur Internet et au laboratoire). Rappelez-vous d'enregistrer les données entre chaque acquisition, sinon elles s'effaceront automatiquement. Le logiciel enregistrera les données sous forme d'un fichier texte qui contient le voltage des différents canaux en fonction du temps. Ces données pourront ensuite être importées dans *Excel* afin d'effectuer le traitement et les analyses.

La manipulation de gaz comprimés nécessite certaines précautions, assurez vous de consulter votre démonstrateur afin de vous y prendre correctement. Veillez à ne pas dépasser une pression de 100 PSIG dans vos montages puisqu'ils n'ont pas été conçus pour soutenir de hautes pressions. Avant de quitter le laboratoire, assurez-vous d'avoir des données de qualité suffisante pour effectuer vos analyses! En tout temps, vous aurez un multimètre *Keithley* à votre disposition. Il s'agit d'un bon outil pour diagnostiquer des problèmes dans votre circuit électrique.

Rapport de laboratoire

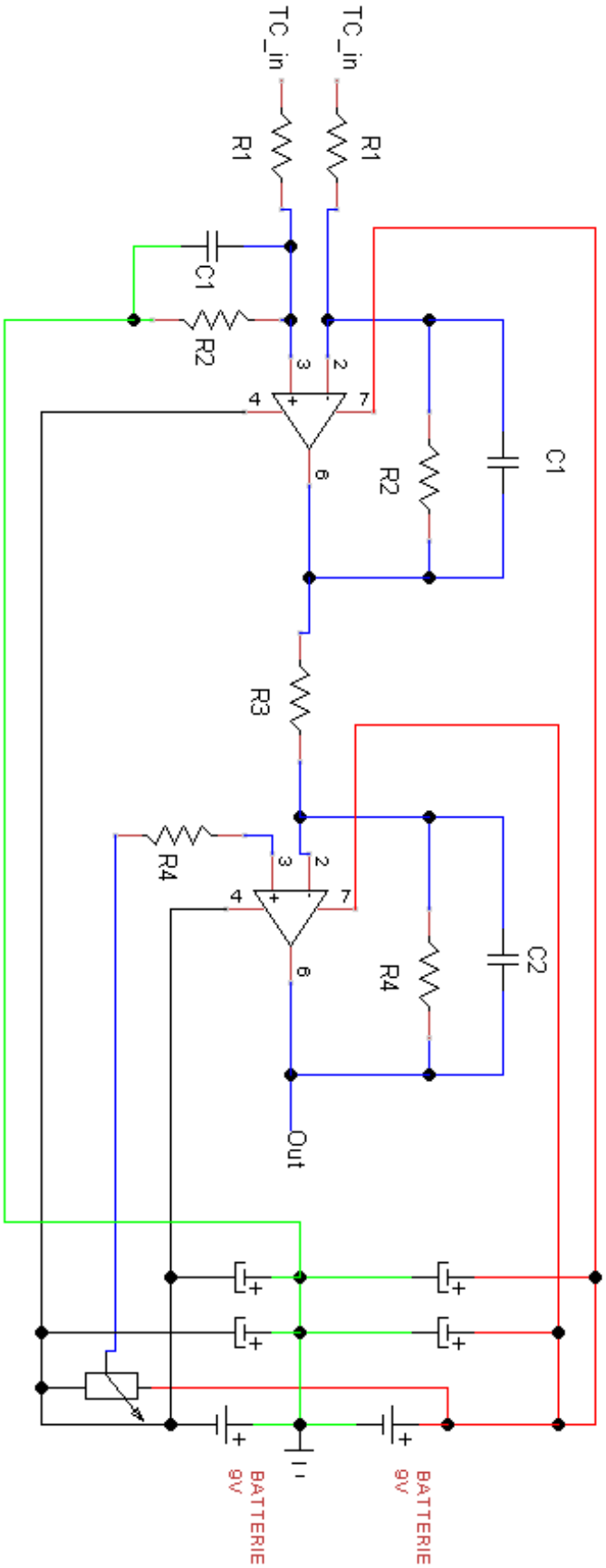
Le rapport de laboratoire devra être produit pendant la période réservée à cet effet. Des directives plus spécifiques vous seront données en temps et lieu.

Liste de documents complémentaires

- *Experiments in Physical Chemistry, 8th Edition*, by Carl W. Garland, Joseph W. Nibler, and David P. Shoemaker, McGraw-Hill, NEW YORK, **2009**. **(EXPÉRIENCE 2)**
- *An improved apparatus for the measurement of the Joule-Thomson coefficient of gases*, A.M Halpern and S. Gozashti, Journal of Chemical Education, **1986** 63 (11), 1001.
- *Physical Chemistry, 6th Edition*, by Ira N. Levine, McGraw-Hill, NEW YORK, **2009**.
- Manuel d'utilisation pour carte d'acquisition FUTEK DAQ-0311A

Voltage(mV) en fonction de la température pour les thermocouples de type T

°C	0	1	2	3	4	5	6	7	8	9	10	°C
-260	-6.232	-6.236	-6.239	-6.242	-6.245	-6.248	-6.251	-6.253	-6.255	-6.256	-6.258	-260
-250	-6.181	-6.187	-6.193	-6.198	-6.204	-6.209	-6.214	-6.219	-6.224	-6.228	-6.232	-250
-240	-6.105	-6.114	-6.122	-6.130	-6.138	-6.146	-6.153	-6.160	-6.167	-6.174	-6.181	-240
-230	-6.007	-6.018	-6.028	-6.039	-6.049	-6.059	-6.068	-6.078	-6.087	-6.096	-6.105	-230
-220	-5.889	-5.901	-5.914	-5.926	-5.938	-5.950	-5.962	-5.973	-5.985	-5.996	-6.007	-220
-210	-5.753	-5.767	-5.782	-5.795	-5.809	-5.823	-5.836	-5.850	-5.863	-5.876	-5.889	-210
-200	-5.603	-5.619	-5.634	-5.650	-5.665	-5.680	-5.695	-5.710	-5.724	-5.739	-5.753	-200
-190	-5.439	-5.456	-5.473	-5.489	-5.506	-5.522	-5.539	-5.555	-5.571	-5.587	-5.603	-190
-180	-5.261	-5.279	-5.297	-5.315	-5.333	-5.351	-5.369	-5.387	-5.404	-5.421	-5.439	-100
-170	-5.069	-5.089	-5.109	-5.128	-5.147	-5.167	-5.186	-5.205	-5.223	-5.242	-5.261	-170
-160	-4.865	-4.886	-4.907	-4.928	-4.948	-4.969	-4.989	-5.010	-5.030	-5.050	-5.069	-160
-150	-4.648	-4.670	-4.693	-4.715	-4.737	-4.758	-4.780	-4.801	-4.823	-4.844	-4.865	-150
-140	-4.419	-4.442	-4.466	-4.489	-4.512	-4.535	-4.558	-4.581	-4.603	-4.626	-4.648	-140
-130	-4.177	-4.202	-4.226	-4.251	-4.275	-4.299	-4.323	-4.347	-4.371	-4.395	-4.419	-130
-120	-3.923	-3.949	-3.974	-4.000	-4.026	-4.051	-4.077	-4.102	-4.127	-4.152	-4.177	-120
-110	-3.656	-3.684	-3.711	-3.737	-3.764	-3.791	-3.818	-3.844	-3.870	-3.897	-3.923	-110
-100	-3.378	-3.407	-3.435	-3.463	-3.491	-3.519	-3.547	-3.574	-3.602	-3.629	-3.656	-100
-90	-3.089	-3.118	-3.147	-3.177	-3.206	-3.235	-3.264	-3.293	-3.321	-3.350	-3.378	-90
-80	-2.788	-2.818	-2.849	-2.879	-2.909	-2.939	-2.970	-2.999	-3.029	-3.059	-3.089	-80
-70	-2.475	-2.507	-2.539	-2.570	-2.602	-2.633	-2.664	-2.695	-2.726	-2.757	-2.788	-70
-60	-2.152	-2.185	-2.218	-2.250	-2.283	-2.315	-2.348	-2.380	-2.412	-2.444	-2.475	-60
-50	-1.819	-1.853	-1.886	-1.920	-1.953	-1.987	-2.020	-2.053	-2.087	-2.120	-2.152	-50
-40	-1.475	-1.510	-1.544	-1.579	-1.614	-1.648	-1.682	-1.717	-1.751	-1.785	-1.819	-40
-30	-1.121	-1.157	-1.192	-1.228	-1.263	-1.299	-1.334	-1.370	-1.405	-1.440	-1.475	-30
-20	-0.757	-0.794	-0.830	-0.867	-0.903	-0.940	-0.976	-1.013	-1.049	-1.085	-1.121	-20
-10	-0.383	-0.421	-0.458	-0.496	-0.534	-0.571	-0.608	-0.646	-0.683	-0.720	-0.757	-10
0	.000	-0.039	-0.077	-0.116	-0.154	-0.193	-0.231	-0.269	-0.307	-0.345	-0.383	0
0	.000	.039	.078	.117	.156	.195	.234	.273	.312	.351	.391	0
10	.391	.430	.470	.510	.549	.589	.629	.669	.709	.749	.789	10
20	.789	.830	.870	.911	.951	.992	1.032	1.073	1.114	1.155	1.196	20
30	1.196	1.237	1.279	1.320	1.361	1.403	1.444	1.486	1.528	1.569	1.611	30
40	1.611	1.653	1.695	1.738	1.780	1.822	1.865	1.907	1.950	1.992	2.035	40
50	2.035	2.078	2.121	2.164	2.207	2.250	2.294	2.337	2.380	2.424	2.467	50
60	2.467	2.511	2.555	2.599	2.643	2.687	2.731	2.775	2.819	2.864	2.908	60
70	2.908	2.953	2.997	3.042	3.087	3.131	3.176	3.221	3.266	3.312	3.357	70
80	3.357	3.402	3.447	3.493	3.538	3.584	3.630	3.676	3.721	3.767	3.813	80
90	3.813	3.859	3.906	3.952	3.998	4.044	4.091	4.137	4.184	4.231	4.277	90
100	4.277	4.324	4.371	4.418	4.465	4.512	4.559	4.607	4.654	4.701	4.749	100
110	4.749	4.796	4.844	4.891	4.939	4.987	5.035	5.083	5.131	5.179	5.227	110
120	5.227	5.275	5.324	5.372	5.420	5.469	5.517	5.566	5.615	5.663	5.712	120
130	5.712	5.761	5.810	5.859	5.908	5.957	6.007	6.056	6.105	6.155	6.204	130
140	6.204	6.254	6.303	6.353	6.403	6.452	6.502	6.552	6.602	6.652	6.702	140
150	6.702	6.753	6.803	6.853	6.903	6.954	7.004	7.055	7.106	7.156	7.207	150
160	7.207	7.258	7.309	7.360	7.411	7.462	7.513	7.564	7.615	7.666	7.718	160
170	7.718	7.769	7.821	7.872	7.924	7.975	8.027	8.079	8.131	8.183	8.235	170
180	8.235	8.287	8.339	8.391	8.443	8.495	8.548	8.600	8.652	8.705	8.757	180
190	8.757	8.810	8.863	8.915	8.968	9.021	9.074	9.127	9.180	9.233	9.286	190
200	9.286	9.339	9.392	9.446	9.499	9.553	9.606	9.659	9.713	9.767	9.820	200
210	9.820	9.874	9.928	9.982	10.036	10.090	10.144	10.198	10.252	10.306	10.360	210
220	10.360	10.414	10.469	10.523	10.578	10.632	10.687	10.741	10.796	10.851	10.905	220
230	10.905	10.960	11.015	11.070	11.125	11.180	11.235	11.290	11.345	11.401	11.456	230
240	11.456	11.511	11.566	11.622	11.677	11.733	11.788	11.844	11.900	11.956	12.011	240
250	12.011	12.067	12.123	12.179	12.235	12.291	12.347	12.403	12.459	12.515	12.572	250
260	12.572	12.628	12.684	12.741	12.797	12.854	12.910	12.967	13.024	13.080	13.137	260
270	13.137	13.194	13.251	13.307	13.364	13.421	13.478	13.535	13.592	13.650	13.707	270
280	13.707	13.764	13.821	13.879	13.936	13.993	14.051	14.108	14.166	14.223	14.281	280
290	14.281	14.339	14.396	14.454	14.512	14.570	14.628	14.686	14.744	14.802	14.860	290
300	14.860	14.918	14.976	15.034	15.092	15.151	15.209	15.267	15.326	15.384	15.443	300
310	15.443	15.501	15.560	15.619	15.677	15.736	15.795	15.853	15.912	15.971	16.030	310
320	16.030	16.089	16.148	16.207	16.266	16.325	16.384	16.444	16.503	16.562	16.621	320
330	16.621	16.681	16.740	16.800	16.859	16.919	16.978	17.038	17.097	17.157	17.217	330
340	17.217	17.277	17.336	17.396	17.456	17.516	17.576	17.636	17.696	17.756	17.816	340
350	17.816	17.877	17.937	17.997	18.057	18.118	18.178	18.238	18.299	18.359	18.420	350
360	18.420	18.480	18.541	18.602	18.662	18.723	18.784	18.845	18.905	18.966	19.027	360
370	19.027	19.088	19.149	19.210	19.271	19.332	19.393	19.455	19.516	19.577	19.638	370
380	19.638	19.699	19.761	19.822	19.883	19.945	20.006	20.068	20.129	20.191	20.252	380
390	20.252	20.314	20.376	20.437	20.499	20.560	20.622	20.684	20.746	20.807	20.869	390


TC_in
TC_in
R1
R1
C1
R2
3
2
4
7
6
R2
C1
R3
R4
3
2
4
7
6
R4
C2
Out
BATTERIE 9V
BATTERIE 9V

SAFETY ISSUES

The ballast bulb must be taped to prevent flying glass fragments in the unlikely event of breakage. Safety glasses should be worn for all laboratory work. Gas cylinders must be chained securely to the wall or laboratory bench (see pp. 644–646 and Appendix C). Liquid nitrogen must be handled properly (see Appendix C).

APPARATUS

Pressure manometer (such as a Honeywell stain-gauge device) and digital voltmeter for readout; properly taped and mounted ballast bulb; heavy-wall pressure tubing; Dewar flask; large ring stirrer; notched cover plate for Dewar with hole for mounting gas thermometer bulb; electrical heating mantle; steam generator with rubber connecting tubing; steam jacket; two ring stands; ring clamp; two clamp holders; one large and one medium clamp.

Cylinder of helium or dry nitrogen; pure ice (1 kg); ice grinder; liquid nitrogen (1 L); boiling chips; stopcock grease; vacuum pump or water aspirator.

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EXPERIMENT 2

Joule–Thomson Effect

The Joule–Thomson effect is a measure of the deviation of the behavior of a real gas from what is defined to be ideal-gas behavior. In this experiment a simple technique for measuring this effect will be applied to a few common gases.

THEORY

An ideal gas may be defined as one for which the following two conditions apply at all temperatures for a fixed quantity of the gas: (1) Boyle's law is obeyed; i.e.,

$$pV = f(T)$$

and (2) the internal energy E is independent of volume. Accordingly, E is independent of pressure as well, and in the absence of other pertinent variables (such as applied fields), E of an ideal gas is therefore a function of the temperature alone:

$$E = g(T)$$

It is apparent that the enthalpy H of an ideal gas is also a function of temperature alone:

$$H \equiv E + pV = h(T)$$

Accordingly, we can write for a definite quantity of an ideal gas at all temperatures

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial p}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T = 0 \tag{1}$$

The absence of any dependence of the internal energy of a gas on volume was suggested by the early experiments of Gay-Lussac and Joule. They found that, when a quantity of gas in a container initially at a given temperature was allowed to expand into another previously evacuated container without work or heat flow to or from the surroundings ($\Delta E = 0$), the final temperature (after the two containers came into equilibrium with each other) was the same as the initial temperature. However, that kind of experiment (known as the *Joule experiment*) is of limited sensitivity, because the heat capacity of the containers is large in comparison with that of the gases studied. Subsequently, Joule and Thomson[1] showed, in a different kind of experiment, that real gases do undergo small temperature changes upon free expansion. This experiment utilized continuous gas flow through a porous plug under adiabatic conditions. Because of the continuous flow, the solid parts of the apparatus come into thermal equilibrium with the flowing gas, and their heat capacities impose a much less serious limitation than in the case of the Joule experiment.

Let it be imagined that gas is flowing slowly from left to right through the porous plug in Fig. 1. To the left of the plug, the temperature and pressure of the gas are T_1 and p_1; and to the right of the plug, they are T_2 and p_2. The volume of a definite quantity of gas (say 1 mol) is V_1 on the left and V_2 on the right, and the internal energy is E_1 and E_2, respectively. When 1 mol of gas flows through the plug, the work done on the system by the surroundings is

$$w = p_1V_1 - p_2V_2$$

Since the process is adiabatic, the change in internal energy is

$$\Delta E = E_2 - E_1 = q + w = w$$

Combining these two equations we obtain

$$E_1 + p_1V_1 = E_2 + p_2V_2$$

or

$$H_1 = H_2 \tag{2}$$

Thus this process takes place at constant enthalpy.

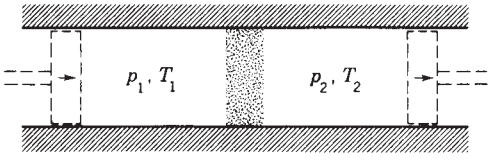

FIGURE 1
Schematic diagram of the Joule–Thomson experiment. The stippled area represents a porous plug.

For a process involving arbitrary infinitesimal changes in pressure and temperature, the change in enthalpy is

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \tag{3}$$

In the present experiment dH is zero and dT and dp cannot be arbitrary but are related by

$$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p} \tag{4}$$

The quantity μ defined by this equation is known as the *Joule–Thomson coefficient.* It represents the limiting value of the experimental ratio of temperature difference to pressure difference as the pressure difference approaches zero:

$$\mu = \lim_{\Delta p \to 0} \left(\frac{\Delta T}{\Delta p}\right)_H \tag{5}$$

Experimentally, ΔT is found to be very nearly linear with Δp over a considerable range; this is in accord with expectations based on the theory given below.

The denominator on the right side of Eq. (4) is the heat capacity at constant pressure C_p. The numerator is zero for an ideal gas [see Eq. (1)]. Accordingly, for an ideal gas the Joule–Thomson coefficient is zero, and there should be no temperature difference across the porous plug. For a real gas, the Joule–Thomson coefficient is a measure of the quantity $(\partial H/\partial p)_T$ [which can be related thermodynamically to the quantity involved in the Joule experiment, $(\partial E/\partial V)_T$]. Using the general thermodynamic relation[2]

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V \tag{6}$$

it can be shown that, for an ideal gas satisfying the criteria already given,

$$pV = \text{const} \times T \tag{7}$$

where T is the absolute thermodynamic temperature. The coefficient $(\partial H/\partial p)_T$ is therefore a measure of the deviation from the behavior predicted by Eq. (7). On combining Eqs. (4) and (6), we obtain

$$\mu = \frac{T(\partial V/\partial T)_p - V}{C_p} \tag{8}$$

In order to predict the magnitude and behavior of the Joule–Thomson coefficient for a real gas, we can use the van der Waals equation of state,[2] which is

$$\left(p + \frac{a}{\tilde{V}^2}\right)(\tilde{V} - b) = RT \tag{9}$$

where $\tilde{V}$ is the molar volume. We can rearrange this equation (neglecting the very small second-order term $ab/\tilde{V}^2$ and substituting p/RT for $1/\tilde{V}$ in a first-order term) to obtain

$$p\tilde{V} = RT - \frac{ap}{RT} + bp$$

Thus,

$$\left(\frac{\partial \tilde{V}}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2}$$

Combination of these two equations yields

$$\left(\frac{\partial \widetilde{V}}{\partial T}\right)_p = \frac{\widetilde{V} - b}{T} + \frac{2a}{RT^2} \tag{10}$$

which on substitution into Eq. (8) gives the expression

$$\mu = \frac{(2a/RT) - b}{\widetilde{C}_p} \quad \text{(van der Waals)} \tag{11}$$

This expression does not contain p or $\widetilde{V}$ explicitly, and the molar heat capacity $\widetilde{C}_p$ may be considered essentially independent of these variables. The temperature dependence of $\widetilde{C}_p$ is small, and accordingly that of μ is also small enough to be neglected over the ΔT obtainable with a Δp of about 1–5 bar (namely about 4 K or less for the gases considered here). Accordingly, we may expect that μ will be approximately independent of Δp over a wide range, as stated previously.

For most gases under ordinary conditions, $2a/RT > b$ (the attractive forces predominate over the repulsive forces in determining the nonideal behavior) and the Joule–Thomson coefficient is therefore positive (gas cools on expansion). At a sufficiently high temperature, the inequality is reversed, and the gas warms on expansion. The temperature at which the Joule–Thomson coefficient changes sign is called the *inversion temperature* T_I. For a van der Waals gas,

$$T_I = \frac{2a}{Rb} \tag{12}$$

This temperature is usually several hundred degrees above room temperature. However, hydrogen and helium are exceptional in having inversion temperatures that are well below room temperatures. This results from the very small attractive forces in these gases (see Table 1 for values of the van der Waals constant a).

TABLE 1 Values of constants in equations of state[a] and the Lennard–Jones potential

	He	H_2	N_2	CO_2
van der Waals[3]:				
a	0.03457	0.2476	1.408	3.640
b	0.02370	0.02661	0.03913	0.04267
Beattie–Bridgeman[4,5]:				
A_0	0.0219	0.2001	1.3623	5.0728
a	0.05984	−0.00506	0.02617	0.07132
B_0	0.01400	0.02096	0.05046	0.10476
b	0.0	−0.04359	−0.00691	0.07235
$10^{-4}c$	0.0040	0.0504	4.20	66.00
Lennard–Jones[6]:				
ϵ/k (K)	6.03	29.2	95.0	189
σ (nm)	0.263	0.287	0.370	0.449

[a] Units assumed are V in $dm^3\ mol^{-1} \equiv L\ mol^{-1}$, p in bar $\equiv 10^5$ Pa, T in K. ($R = 0.083145$ bar $dm^3\ K^{-1}\ mol^{-1}$.)

Other semiempirical equations of state can be used to predict Joule–Thomson coefficients. Perhaps the best of these is the Beattie–Bridgeman equation,[4,5] which can be written (for 1 mol) as

$$p = \frac{RT(1-\epsilon)}{\tilde{V}^2}(\tilde{V} + B) - \frac{A}{\tilde{V}^2} \tag{13}$$

where $A = A_0(1 - a/\tilde{V})$, $B = B_0(1 - b/\tilde{V})$, and $\epsilon = c/\tilde{V}T^3$. In this equation of state, there are five constants which are characteristic of the particular gas: A_0, B_0, a, b, and c. In terms of these constants and the pressure and temperature, the Joule–Thomson coefficient is given[4] by

$$\mu = \frac{1}{\tilde{C}_p}\left\{-B_0 + \frac{2A_0}{RT} + \frac{4c}{T^3} + \left[\frac{2B_0 b}{RT} - \frac{3A_0 a}{(RT)^2} + \frac{5B_0 c}{RT^4}\right]p\right\} \tag{14}$$

This equation predicts a small dependence on pressure not shown by Eq. (11), which is based on the van der Waals equation.

The most general of the equations of state is the *virial equation,* which is also the most fundamental since it has a direct theoretical connection to the intermolecular potential function. The virial equation of state expresses the deviation from ideality as a series expansion in density and, in terms of molar volume, can be written

$$\frac{p\tilde{V}}{RT} = 1 + \frac{B_2(T)}{\tilde{V}} + \frac{B_3(T)}{\tilde{V}^2} + \ldots \tag{15}$$

The virial coefficients B_2 and B_3 depend only on temperature and are determined by two- and three-body interactions between molecules, respectively. For pressures below about 10 bar, the B_3 term is very small and can be neglected. Solving Eq. (15) for $\tilde{V}$ and $(\partial\tilde{V}/\partial T)_p$ in a manner similar to that for the van der Waals case above gives

$$\mu = \frac{T(\partial B_2/\partial T)_p - B_2}{\tilde{C}_p} \tag{16}$$

From statistical mechanics,[6] $B_2(T)$ is given by

$$B_2(T) = N_0\int_0^\infty [1 - e^{-U(r)/kT}]2\pi r^2\, dr \tag{17}$$

and $(\partial B_2/\partial T)_p$ can be obtained by differentiation. $U(r)$ is the potential energy as a function of the separation of the molecules, taken to be spherical, and is important because it can be used to predict many of the transport and collisional properties of a molecule. One common choice for $U(r)$ is the so-called Lennard–Jones 6-12 potential, which has the form

$$U(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{18}$$

where ε is the well depth corresponding to the minimum in the potential and σ is the separation corresponding to $U(r) = 0$; see Fig. 47-1. Values for these parameters are included in Table 1 for the gases of interest in this experiment.

EXPERIMENTAL

The experimental apparatus shown in Fig. 2 is patterned after a design given in Ref. 7. The "porous plug" is a $\frac{3}{8}$-in.-OD stainless steel frit of 2 μm pore size and $\frac{1}{16}$-in. thickness pressed into a $\frac{3}{8}$-in. Swagelok tee made of nylon for reduced thermal conductivity.

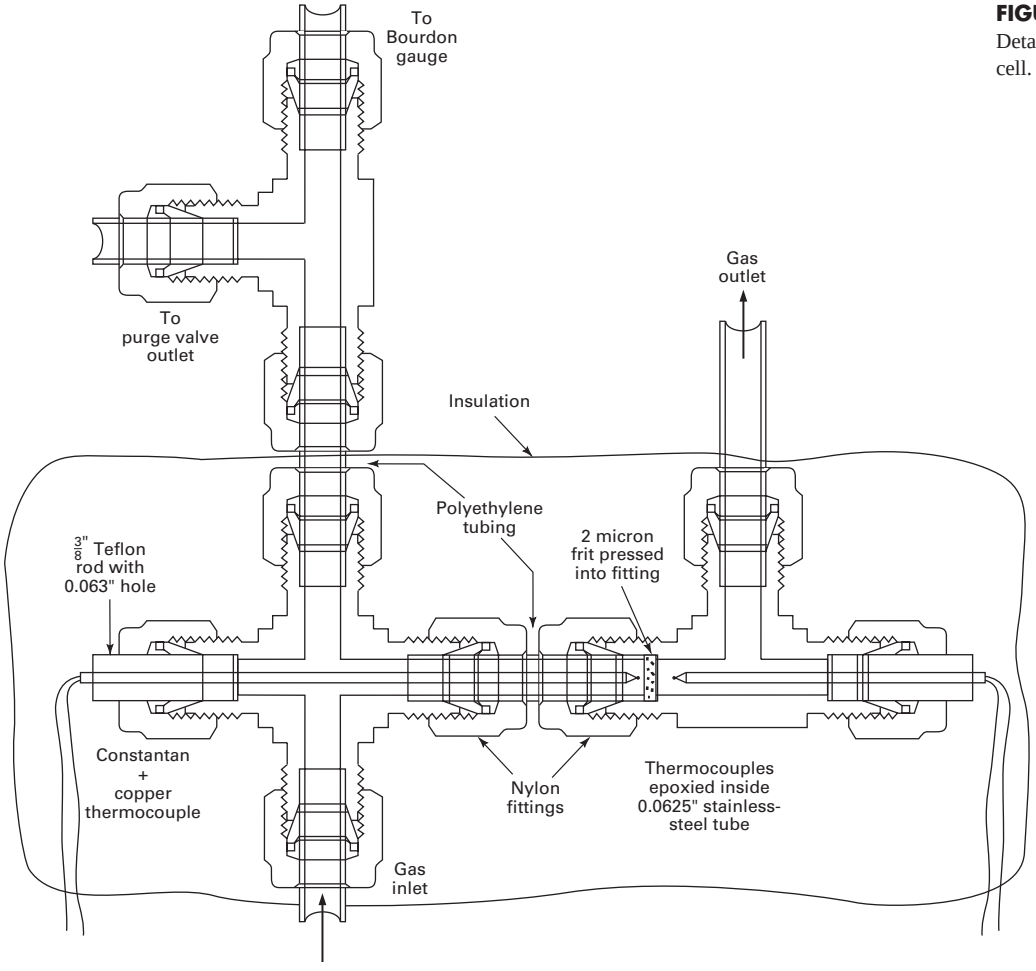

FIGURE 2
Detail of Joule–Thomson cell.

The high-pressure inlet is attached to a $\frac{3}{8}$-in. cross to provide ports for gas introduction, pressure measurement, and thermocouple placement just in front of the frit. The Bourdon gauge (0–10 bar) should be connected via a tee to a purge valve to facilitate gas changes. Before use the assembly should be tested at 10 bar for leaks. Thermal insulation such as glass wool should be wrapped around the frit assembly to keep the expansion as adiabatic as possible.

The temperature difference ΔT across the frit is measured with two copper-Constantan (type T) thermocouples with wires of 0.010-in. diameter or less for reduced thermal conductivity. The thermocouples can be sealed with epoxy into a $\frac{1}{16}$-in. stainless-steel sheathing tube, which can be connected to the cross fitting by a $\frac{1}{16}$-in. to $\frac{3}{8}$-in. Swagelok adaptor, or more simply by swaging a $\frac{3}{8}$-in. Teflon rod with a 0.063-in. feedthrough hole for the thermocouple tube, as shown in Fig. 2. A convenient 6-in., $\frac{1}{16}$-in.-OD sealed subminiature probe with an exposed thermocouple junction and external strain relief is available from Omega (e.g., probe TMTSS-062E-6). The 6-in. length is sufficient to allow the thermocouples to be positioned adjacent to the center of the frit, as shown in the figure.

Because the maximum temperature change will be only 0.5 to 4 K, a sensitive digital voltmeter (0.1 μV), null voltmeter, or potentiometer is desirable for accurate measurements. To obtain the temperature *difference* directly, the two Constantan leads of the thermocouples

should be clamped together and the copper leads should be attached to the measuring device.† For best absolute accuracy, the two thermocouples should be calibrated (e.g., using a standard thermometer) to determine their temperature coefficients (Seebeck coefficient) α. However, for a copper–Constantan thermocouple, α varies only slightly with temperature, from 39 to 43 μV K^{-1} from 0 to 50°C. At 25°C, α is 40.6 μV K^{-1} and the variation is small from one thermocouple to another. For small temperature differences, a linear relation $\Delta V_{TC} = \alpha \Delta T = \alpha(dT/dP)\Delta p$ is a good approximation for the thermocouple potential difference between the two junctions.‡ Thus, to the accuracy needed for this experiment, the slope of a plot of ΔV_{TC} versus Δp can be combined with an assumed value of $\alpha = 40.6$ μV K^{-1} to yield (dT/dp) and hence μ.

Procedure. Set up the apparatus shown in Fig. 2. The gas supply should be a cylinder or supply line equipped with a pressure regulator and a control valve. The supply pressure should be constant during the measurements. Because a significant temperature change occurs as gases go from high to low pressure through the pressure regulator itself, the gas should be passed through about 50 ft of $\frac{1}{4}$-in. coiled copper tubing contained in a water bath at 25 ± 1°C. A $\frac{1}{4}$-in.-to-$\frac{3}{8}$-in. adaptor can be used for a short, insulated polyethylene tubing connection to the expansion apparatus. Before initiating gas flow, record the bath temperature and determine any offset voltage between the two thermocouples.

Start the measurements with CO_2 with the pressure regulator set to minimum pressure. Open the control valve and purge the copper line and pressure gauge of air or any other gases with the purge valve open. Then close the purge valve and slowly increase the pressure to 4 bar. After this pressure is reached, record the thermocouple reading every 30 s, until the values become constant (typically a few minutes). Lower the regulator pressure by about 0.5 bar and again take readings every 30 s until a constant value is obtained. Continue this procedure down to a final pressure of 0.5 bar. Note that this is the excess pressure over the discharge pressure into the room (assumed to be at 1 bar).

Change the gas supply to N_2 and again purge the copper coil and pressure gauge with the purge valve open. Close this valve and bring the pressure slowly to 10 bar, a higher value than for CO_2 since the cooling is less. After the temperature has stabilized, repeat the sequence of measurements as for CO_2 but at 1-bar intervals. Finally, repeat the N_2 procedure using He gas. In this case, the temperature change will be much smaller and positive: i.e., the gas heats on expansion because it is above the so-called Joule–Thomson inversion point, the temperature at which the coefficient μ is zero. After completion of the experiment, make sure that all cylinder valves are closed.

CALCULATIONS

For each gas studied, do a linear regression to fit ΔV_{TC} (or ΔT) versus Δp so as to obtain the slope along with its standard error. On a single graph, show for each of the three gases the best-fit straight line along with the experimental data points. From the slopes, evaluate the Joule–Thomson coefficient μ in units of K bar^{-1}. Compare your results with literature values given in Ref. 7. Calculate μ for these gases at 25°C from the van der

†As an alternative to a thermocouple, one can use two sensitive thermistor probes and an appropriate resistance bridge circuit (see Chapters XVI and XVII). A calibration to convert the bridge measurement to ΔT is required in this case.

‡In practice, one often finds that $\Delta V_{TC} = \alpha \Delta T + \delta V_{TC}$, where δV_{TC} is a small offset voltage (~1–3 μV) observed when both the reference and the measuring junction are at the same temperature. This "nonthermodynamic" result can occur if the thermocouple wire has regions of compositional variation or strain (e.g., from kinking) that are subject to a temperature gradient. δV_{TC} can be ignored in this experiment, since it affects only the intercept of the plot of ΔV_{TC} versus Δp and not the slope.

Waals and Beattie–Bridgeman constants given in Table 1. $\widetilde{C}_p$ values for He, N_2, and CO_2 at 25°C are 20.79, 29.12, and 37.11 J K^{-1} mol^{-1}, respectively.

Plot the Lennard–Jones potentials for each of the gases studied. Obtain μ from Eqs. (16)–(18) by numerical integration and compare the values from this two-parameter potential with those from the van der Waals and Beattie–Bridgeman equations of state. [*Optional:* A simple square-well potential model can also be used to crudely represent the interaction of two molecules. In place of Eq. (18), use the square-well potential and parameters of Ref. 6 to calculate μ. Contrast with the results from the Lennard–Jones potential and comment on the sensitivity of the calculations to the form of the potential.]

DISCUSSION

The Joule–Thomson coefficient gives a measure of how much potential energy is converted into kinetic energy or vice versa as molecules in a dense gas change their average separation during an adiabatic expansion. As mentioned earlier, the magnitude and sign of μ are determined by the balance of attractive and repulsive interactions and, for most gases at room temperature, cooling occurs as molecules work against a net attractive force as they move apart. The exceptions are the weakly interacting species He and H_2, where μ is negative at 300 K and precooling below the inversion temperature is first necessary before cooling can occur on expansion. Calculate the inversion temperature for the gases of Table 1 using Eqs. (11), (14), and (16), neglecting the last, small pressure-dependent term in (14), and compare your values with experimental ones you find in the literature. Equations (14) and (16) can be most easily solved for T_I by iteration, using for example the Solve For function of spreadsheet programs, as discussed in Chapter III.

Joule–Thomson cooling is the basis for the Linde method of gas liquefaction, in which a gas is compressed, allowed to cool by heat exchange, and is then expanded to cool sufficiently that the gas liquefies. This effect is also important in the operation of refrigerators and heat pumps. Using cylinders of high-pressure gas, cooling can be achieved without power input in a device without moving parts, and hence the Joule–Thomson process has been used in cooling of small infrared and optical detectors on space probes. Discuss some of the design factors that might be important in achieving maximum cooling efficiency in the latter kind of a device.

For the more difficult Joule experiment, we can write

$$\eta \equiv -\left(\frac{\partial T}{\partial V}\right)_E = \frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = \frac{T(\partial p/\partial T)_V - p}{C_v} \tag{19}$$

This quantity is called the *Joule coefficient.* It is the limit of $-(\Delta T/\Delta V)_E$, corrected for the heat capacity of the containers as ΔV approaches zero. With the van der Waals equation of state, we obtain $\eta = a/\widetilde{V}^2\widetilde{C}_v$. The corrected temperature change when the two containers are of equal volume is found by integration to be $\Delta T = -a/2\widetilde{V}\widetilde{C}_v$, where $\widetilde{V}$ is the initial molar volume and $\widetilde{C}_v$ is the molar constant-volume heat capacity. It is instructive to calculate this ΔT for a gas such as CO_2. In addition, the student may consider the relative heat capacities of 10 L of the gas at a pressure of 1 bar and that of the quantity of copper required to construct two spheres of this volume with walls (say) 1 mm thick and then calculate the ΔT expected to be observed with such an experimental arrangement.

SAFETY ISSUES

Gas cylinders must be chained securely to the wall or laboratory bench (see pp. 644–646 and Appendix C).

APPARATUS

Insulated Joule–Thomson cell similar to that of Fig. 2 (suitable stainless steel frits can be obtained from chromatographic parts suppliers, e.g., Upchurch Scientific part C-414); metal or nylon tees, crosses, and reducers (available from Swagelok and other manufacturers); $\frac{3}{8}$-in. Teflon rod; type T insulated copper–Constantan thermocouples with 0.010-in.-diameter wires; voltmeter with 0.1-μV resolution (e.g., Keithley 196), null voltmeter (e.g., Hewlett Packard 419A or Keithley 155), or sensitive potentiometer (e.g., Keithley K-3). Cylinders of CO_2, N_2, and He with regulators and control valves; 50 ft of $\frac{1}{4}$-in. copper coil, $\frac{3}{8}$-in. and $\frac{1}{4}$-in. polyethylene tubing; 0- to 10-bar Bourdon gauge; 25°C water bath.

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EXPERIMENT 3

Heat-Capacity Ratios for Gases

The ratio C_p/C_v of the heat capacity of a gas at constant pressure to that at constant volume will be determined by either the method of adiabatic expansion or the sound velocity method. Several gases will be studied, and the results will be interpreted in terms of the contribution made to the specific heat by various molecular degrees of freedom.

THEORY

In considering the theoretical calculation of the heat capacities of gases, we shall be concerned only with perfect gases. Since $\tilde{C}_p = \tilde{C}_v + R$ for an ideal gas (where $\tilde{C}_p$ and $\tilde{C}_v$ are the molar quantities C_p/n and C_v/n), our discussion can be restricted to C_v.

An Improved Apparatus for the Measurement of the Joule-Thomson Coefficient of Gases

Arthur M. Halpern and Saeed Gozashti
Northeastern University, Boston, MA 02115

One of the common applications of real gases presented in undergraduate treatments of thermodynamics is the Joule-Thomson (JT) effect. This topic not only explicitly shows how a nonzero JT coefficient arises from an equation of state for a real gas, but it also appeals to the student's physical experience with the cooling associated with most expanding gases. In addition, the ability to calculate the JT coefficient (μ_{JT}) from an equation of state illustrates the computational nature of thermodynamics as well as the relative utility of equations of state.

Experimental measurements of μ_{JT} nicely fit into the laboratory portion of physical chemistry. Accordingly, this experiment is described in Shoemaker et al. (*1*). The procedure described there, however, is awkward and probably lacks the sensitivity needed to observe and quantitatively to measure the effect for He. A somewhat different approach was described by Hecht and Zimmerman (*2*), but this procedure, while an improvement, is also unwieldy and may not work satisfactorily with He. One of the drawbacks with these apparatus is the need to construct specialized and cumbersome equipment.

In this paper, we describe an apparatus that can be constructed from commercially available components and that has the sensitivity to measure μ_{JT} for He with reasonable accuracy. The strategy is to use gas fittings and a porous plug made from stainless steel. This material was chosen because of its lower thermal conductivity (relative to brass). Unlike the glass used in the JT cells previously described, our stainless steel apparatus can withstand higher pressures, and, in the case of He, this contributes to the ability to measure μ_{JT} with reasonable accuracy. The two commonly used gases N_2 and CO_2 are easily studied with this apparatus. In addition, SF_6 is used; it is a good choice for this experiment because it is presumably nontoxic, nonreactive, and relatively inexpensive. Moreover, there is considerable interest in this material as a dielectric and possible refrigerant and as a model for multiple infrared photon absorption. The students can thus made aware of this information.

A diagram of this apparatus is shown in Figure 1. The heart of the high-pressure part of the JT cell is a $\frac{3}{8}$-in. union cross (Swagelok SS-600-4) adapted on three sides to $\frac{1}{8}$-in. (SS-200-R-6). The gas inlet is coupled via a $\frac{1}{8}$-in. Teflon tube and the pressure is read via a 0–100 psi gauge also connected by $\frac{1}{8}$-in. Teflon tubing (used to reduce heat transfer to/from the JT cell). A copper/constantan thermocouple, sealed with an epoxy adhesive passes through a $\frac{1}{8}$-in. tube and is positioned in the center of the interior of the cross. This thermocouple is constructed from narrow gauge leads (0.010 in.) also to reduce heat transfer (Omega Engineering Inc). The expansion plug (2 μm) used was a $\frac{3}{8}$-in. stainless steel HPLC bed support (43-38BS, Rainin Inst. Co.). The frit is contained in a $\frac{3}{8}$-in. union (SS-600-6); the latter is connected to the cross via a $\frac{3}{8}$-in. close-couple. The low-pressure thermocouple is fed through a #17 stainless steel syringe needle (the sharp end removed) as a guide and held rigid by a $\frac{3}{8}$–$\frac{3}{16}$-in. reducing union (ss-600-6-1) with Teflon ferrules. The gas outlet is provided by several holes drilled through a short length (2 in.) of $\frac{3}{8}$-in. tubing placed between the frit-containing union and the reducing union. To damp out fluctuations in the temperature difference read by the thermocouples, the low-pressure thermocouple was fastened to a small brass cup attached to the end of the guide using a minute amount of epoxy adhesive, heavily impregnated with brass filings to improve the thermal conductivity. The cup was prepared by simply filing down the lock-end of the syringe. To provide additional insulation, a short length of Tygon tubing is inserted into the high-pressure side of the frit. Holes are provided for the thermocouple and pressure gauge. Finally, to keep the entire apparatus as adiabatic as possible, it was wrapped in several layers of glass wool.

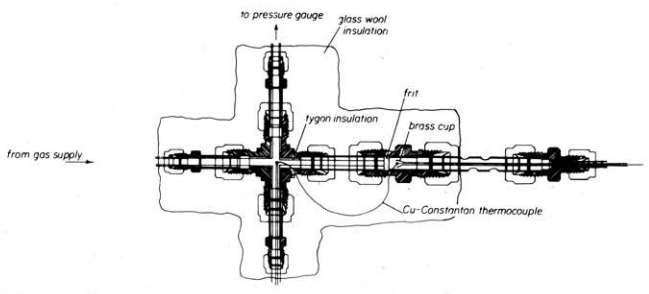

Figure 1. Cut-away diagram of the apparatus. The stainless steel fittings and other components are described in the text.

The two thermocouples were found to be very well matched so that when connected in series to indicate the temperature difference between them, an immeasurably small potential was observed when they were isothermally equilibrated. As an indication of the thermal balance between the thermocouples, the voltage of the equilibrated, static apparatus was usually found to be less than 1 μv. Best results were obtained under this condition which could be brought about by a very slow trickle of gas (He or N_2) through the apparatus. The potential developed by the thermocouples was directly read by a Hewlett-Packard model 419A null voltmeter. Alternatively, another readout device having an appropriately high input resistance can be used. A calibration of 39 μV/°C (confirmed by the freezing point of benzene) was used in these experiments.

The measurements for He were carried out between pressures of 90 and 30 psi. Stable voltages were established after about 15–30 s. Readings were taken in increments of 10 psi. For the other gases where the JT effect is larger, the highest pressure used could be reduced. The entire experiment involving the measurement of the four gases can be carried out in less than 3 h.

The JT coefficients were determined by a linear regression of the data, (see Fig. 2) assuming a low-pressure value of 1 atm. The highest pressure used is low enough to justify the assumption of P-independent JT coefficients. These were compared with μ_{JT} as calculated from three equations of state: van der Waals (vdW), Redlich-Kwong (RK) (*3*, *4*) and Beattie-Bridgeman (BB) (*5*, *6*). The results are shown in the table. The first two involve two parameters which can be obtained from critical data while the latter incorporates five empirical parameters.

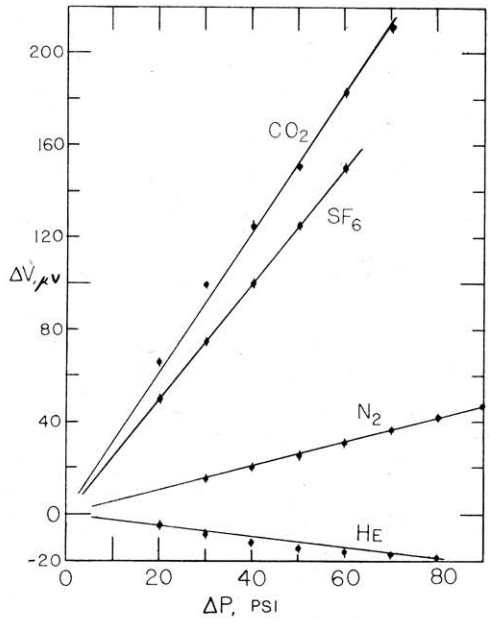

Figure 2. Plots of ΔV versus ΔP for the gases studied: He, N_2, SF_6, and CO_2. The ambient temperature is 298 K.

Critical Data, Heat Capacities, vdW, RK,and BB Parameters for He, N_2, CO_2, and SF_6 (*9*), as well as Calculated, Measured, and Literature Values (*10*, *11*) for μ_{JT}

	He	N_2	SF_6	CO_2	
V_c	0.0578	0.0901	0.199	0.0940	dm^3/mol
P_c	2.261	33.54	37.11	72.85	atm
T_c	5.20	126.27	318.71	304.20	K
C_P	0.2052	0.2875	0.9602	0.366	dm^3-atm mol-K
a(vdW)	0.03397	1.350	7.775	3.609	
b(vdW)	0.02359	0.03862	0.08809	0.04283	
a (RK)	0.07851	15.38	140.7	63.78	
b (RK)	0.01635	0.02677	0.06106	0.02969	
A_0	0.0216	1.3445	...	5.0065	
B_0	0.0140	0.05046	...	0.07235	
C	40	4.20×10^4	...	6.600×10^5	
μ_{JT}(vdW)	−0.101	0.250	0.571	0.689	
μ_{JT}(RK)	−0.0774	0.224	0.804	0.951	
μ_{JT}(BB)	−0.0596	0.229	...	1.10	
μ_{JT}(meas)	−0.066	0.230	0.968	1.07	
μ_{JT}(lit)	−0.0624	0.2217	0.962	1.10	

The well-known vdW equation is

$$P = RT/(V - b) - a/V^2 \quad (1)$$

and the RK equation, which is a very useful two parameter state function reads

$$P = RT/(V - b) - a/\{V(V + b)T^{1/2}\} \quad (2)$$

The vdW a and b parameters expressed in terms of the critical temperature, T_c, and pressure P_c, are

$$a = 2.8408 \times 10^{-3} T_c^{\,2}/P_c$$

and

$$b = 0.010257 T_c/P_c \quad (3)$$

where units of dm^3, atm, and K are implied.

Likewise, for the RK equation

$$a = 2.879 \times 10^{-3} (T_c^{\,5/2})/P_c$$

and

$$b = 7.1097 \times 10^{-3} T_c/P_c$$

The BB equation, containing the five parameters, a, b, A_0, B_0, and c is

$$P = RT\{1 - c/VT^3\}\{V + B_0(1 - b/V)\}/V^2 - A_0(1 - a/V)/V^2 \quad (4)$$

The BB equation can be cast into the more convenient virial form (*6*),

$$P = RT/VT + (RT/V^2)\{B_0 - A_0/(RT) - c/T^3\} + (RT/V^3)\{-B_0 b + A_0 a/(RT) - B_0 c/T^3\} + (RT/V^4)(B_0 bc/T^3) \quad (5)$$

The JT coefficient, defined as $(\partial T/\partial p)_H$ can be expressed in terms of the T and V partial derivatives of the equation of state explicit in P (see also *7*, *8*),

$$\mu_{JT} = (1/C_P)\{-T(\partial p/\partial T)_V/(\partial p/\partial V)_T - V\} \quad (6)$$

The application of equation 6 to the vdW, RK, and BB equations of state provides, in the limit of large V, the following V-independent expressions for μ_{JT}:

$$\mu_{JT} = (1/C_P)\{2a/(RT) - b\} \quad (vdW) \quad (7)$$

$$\mu_{JT} = (1/C_P)\{5a/(2RT^{3/2}) - b\} \quad (RK) \quad (8)$$

$$\mu_{JT} = (1/C_P)\{2A_0/(RT) + 4c/T^3 - B_0\} \quad (BB) \quad (9)$$

The values of μ_{JT}, calculated from eqs 7–9 along with those measured with the apparatus described are listed in the table, which also contains the literature values as well as the critical constants of the gases. As can be seen, the agreement is quite satisfactory and demonstrates the sensitivity and accuracy attainable with this simple apparatus.

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